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MULLITE-TIALITE CERAMIC MATERIALS BASED ON CHEMICALLY PRECIPITATED MIXTURES (A REVIEW)

N. F. Popovskaya[1] and N. M. Bobkova[1]

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The present state of production of heat-resistant refractory technical ceramics is described. The optimum synthesis conditions and the properties of mullite-tialite ceramic materials based on chemically precipitated mixtures are identified.

The intense development of new technologies for producing inorganic materials is related to the demand for materials that have high strength, wear, and heat resistance, and stable mechanical and thermophysical properties under conditions of abruptly varying temperatures.

The demand for high-temperature materials is satisfied by using technical ceramics, in particular, ceramics based on aluminum titanate $Al_2O_3 \cdot TiO_2$ (tialite), which has a number of valuable properties: high fire and heat resistance due to an elevated melting temperature (1890°C) and a low TCLE ($-19 \cdot 10^{-7}\,K^{-1}$). However, tialite ceramics due to their low sinterability have low mechanical strength, which can be increased by introducing a reinforcing phase, for instance, mullite $3Al_2O_3 \cdot 2SiO_2$. This phase has strength, fire resistance, and chemical resistance values with a medium-level TCLE.

Among the promising methods for producing powder for the synthesis of mullite-tialite ceramics with high thermomechanical parameters are chemical precipitation methods. Their specifics make it possible to produce powders of complex chemical compositions and control their microstructure by controlling the precipitation conditions, during which the mixing process takes place at the molecular level. This enables one to lower the temperature of synthesis and to improve the quality of ceramic materials obtained from such powders, which results in the higher cost of raw materials involved in the chemical method.

The formation regularities and properties of mullite-tialite ceramics based on chemically precipitated mixtures are little studied, although interest in this ceramic is evident. There are some publications related to the production of mullite-tialite ceramics by the traditional method (Japan Patent application 62-2756, USSR Inventor’s Certif. No. 1218362) [1 – 8]. All authors observe high thermomechanical properties of mullite-tialite ceramics.

The improved thermomechanical properties of ceramics based on the $Al_2O_3 - SiO_2 - TiO_2$ system are determined by their phase composition and morphological specifics. The needle-shaped structure of mullite ensures a high mechanical strength of materials, and the fine-crystalline structure of tialite under low TCLEs ensures high thermal resistance. However, the production of ceramic materials using pure aluminum, silicon and titanium oxides and mixtures of previously synthesized tialite or mullite involves a substantial consumption of energy (fine milling, high firing temperatures, a two-stage synthesis of tialite [9], etc.)

Therefore the possibility of producing initial mixtures by chemical methods is interesting. The authors of [10] describe a mullite-tialite composite material synthesized by the sol-gel method at temperatures of 800 – 1300°C and exhibiting high strength and stability of properties. However, there are virtually no data on the production of mullite-tialite ceramics by a more accessible method, i.e., by chemical precipitation.

To determine the optimum ratio for mixtures of tialite and mullite, we constructed an estimated phase diagram of a mullite-tialite composition. The calculation was performed using the Schroeder – Le Chatelier equations. Theoretically, a eutectic tialite-mullite composition correlates with a ratio of 46% tialite to 54% mullite and a temperature of 1665°C. Since the sintering of materials of eutectic composition is expected to be carried out at a lower temperature, a tialite : mullite ratio close to the eutectic composition was selected for further studies.

The earlier studies of the materials based on aluminum titanate and mullite [11 – 17] synthesized by the chemical precipitation method made it possible to select the optimum powder preparation conditions for each system.

The precipitate in mixtures of $AlCl_3 - Na_2SiO_3$ and TiO_2 solutions was prepared by different methods (ATS-1 and ATS-2). The precipitate was washed to remove extraneous ions and dried to a constant mass.

[1] Belarus State Technological University, Minsk, Belarus.

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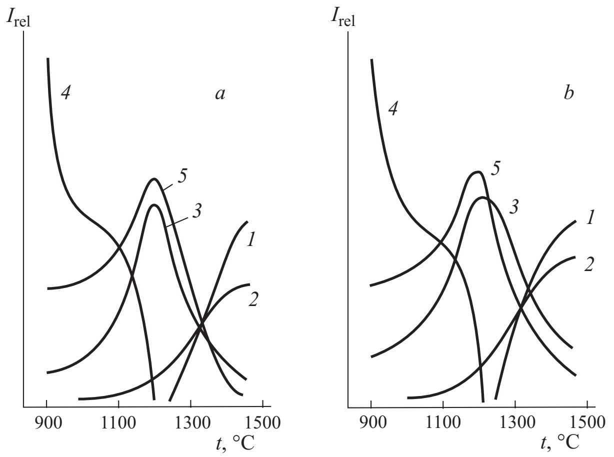

Fig. 1. Sequence of formation of crystalline phases under heat treatment of samples made from the precipitates ATS-1 (*a*) and ATS-2 (*b*): *1*) tialite ($d = 0.335$ nm); *2*) mullite ($d = 0.339$ nm); *3*) corundum ($d = 0.208$ nm), *4*) anatase ($d = 0.351$ nm); *5*) rutile ($d = 0.324$ nm).

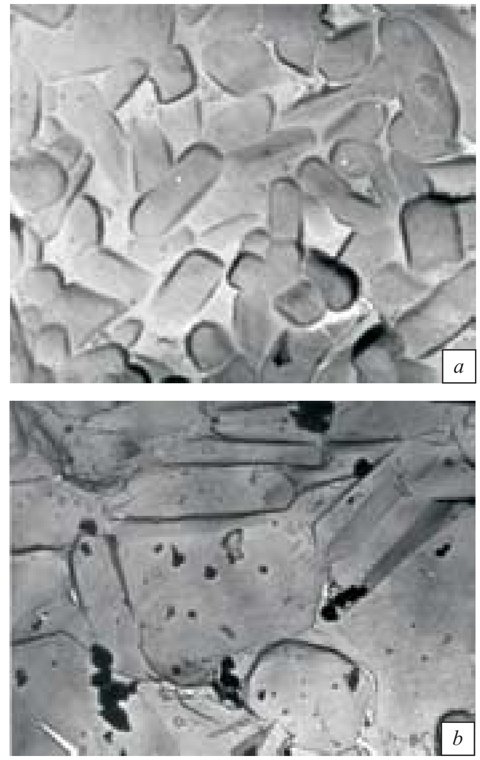

Fig. 2. Electron microscope studies of a fracture of mullite-tialite ceramic at magnification of 19,000 (*a*) and 12,000 (*b*) times.

To study the phase composition and identify the optimum synthesis conditions, samples with a plastifying additive were molded by compression and fired under various temperature-time conditions. The phase composition of the ceramics was determined by x-ray phase analysis.

The quantitative variations in the crystalline phases can be estimated based on the intensity of the main diffraction peaks. The sequence of formation of the crystalline phases in heat treatment of the samples reflects the variations of the peak intensities on the x-ray patterns (Fig. 1).

Titanium dioxide in the ATS-1 sample is represented by anatase, which persists up to a temperature of 900°C; then its quantity sharply decreases due to the transformation of anatase into rutile. A complete transformation of anatase into rutile occurs within a temperature interval of 1100 – 1200°C. Active crystallization of corundum starts at a temperature of 900°C.

Mullite emerges within a temperature interval of 950 – 1000°C, and its content sharply increases after heat treatment at 1300°C. The beginning of the formation of tialite is registered only within a temperature interval of 1250 – 1300°C. After heat treatment at 1450°C, the main phases in the material are mullite and tialite, while a certain quantity of rutile and corundum that have not reacted is preserved.

The regularities of phase transformations in the ATS-2 samples are approximately the same; however, the content of rutile and corundum that have not entered into the reactions is somewhat higher in the end product, i.e., the method of obtaining a precipitate has an effect on the phase composition of the end product of firing. The phase formation is completed at a temperature of 1450°C after a 2-h exposure.

The study of the microstructure of samples fired at a temperature of 1450°C with 2-h exposure at the maximum temperature was carried out with an electron microscope on fractures of ceramic samples (Fig. 2). Their structure consists of elongated mullite crystals and round tialite crystals with a

TABLE 1

Parameter	ATS-1 ceramics	Ceramics produced by the traditional technologies, published sources		
		[6]	USSR Inventor's Certif. No. 1218362	[8]
Water absorption, %	7 – 9	7 – 13	–	–
Compression strength, MPa	96 – 98	31 – 77	65 – 69	–
TCLE, 10^{-7} K^{-1}	10 – 12	12 – 21	28 – 39	20 – 50
Heat resistance, number of thermal cycles, °C:				
1000 – 20	> 100	80 – 90	–	–
350 – 20	–	–	100	–
Preliminary synthesis of mullite and tialite	None	None	None	Is used*
Firing temperature, °C	1400 – 1450	1400 – 1450	1360 – 1400	–

* Tialite was synthesized at a temperature of 1550 – 1600°C, and mullite was obtained from high-alumina chamotte.

very uniform distribution of crystals and an insignificant difference in sizes. As the crystals do not have a large size, the level of internal stresses is low and, accordingly, microcracks do not arise in firing.

Heterophase precipitation using TiO_2 made it possible to substantially (7 – 8 times) increase the precipitate filtration coefficient, compared with the precipitate obtained in the $AlCl_3 - Na_2SiO_3$ system. The measured filtration coefficient of the ATS-1 samples is equal to 7.39×10^{-7} cm/sec and that of the $AlCl_3 - Na_2SiO_3$ system is equal to 0.89×10^{-7} cm/sec. A one-day aging as well increases the filtration coefficient 1.3 – 1.5 times. The physicochemical properties of the synthesized ceramic material compared to the properties of mullite-tialite materials obtained by the traditional technology are listed in Table 1.

A comparison of the listed data shows that the synthesized ceramic material has a significantly higher strength and a lower TCLE, which facilitates better thermomechanical properties.

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